Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

BaClBF4: A New Noncentrosymmetric Pseudo-Aurivillius Type Material with Transparency Range from Deep UV to Middle IR and High Laser Damage Threshold

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Table S1. Atomic coordinates, equivalent isotropic displacement parameters (A^2) and bond valence sum for $BaClBF_4$. *U*(eq) is defined as one third of the trace of the orthogonalized *U*ij tensor.

Atoms	Wyckoff positions	*x*	*y*	*z*	*U*(eq)	BVS
Ba(1)	2*a*	1.0000	0.7020(1)	-0.0223	0.014(1)	2.189
Cl(1)	2*a*	1/2	0.5185(1)	-0.0151(8)	0.016(1)	1.193
B(1)	2*a*	1/2	0.8673(8)	0.4030(16)	0.020(2)	3.156
F(1)	2*a*	1/2	0.8561(5)	0.1041(11)	0.031(1)	0.885
F(2)	4*b*	1.2811(6)	0.7988(2)	0.4680(40)	0.034(1)	1.102
F(3)	2*a*	1/2	1.0085(3)	0.4770(30)	0.034(1)	1.040

Table S2. Selected bond angles (deg) for $BaClBF_4$.[b]

F(3)#1-Ba(1)-F(2)#2	71.8(3)	F(2)#4-Ba(1)-Cl(1)	126.2(2)
F(2)-Ba(1)-F(2)#2	61.1(4)	F(1)#5-Ba(1)-Cl(1)	167.27(10)
F(3)#1-Ba(1)-F(2)#3	72.2(3)	F(1)-Ba(1)-Cl(1)	62.60(10)
F(2)-Ba(1)-F(2)#3	144.00(9)	Cl(1)#6-Ba(1)-Cl(1)	69.19(4)
F(2)#2-Ba(1)-F(2)#3	107.79(10)	F(3)#1-Ba(1)-Cl(1)#5	123.28(3)
F(3)#1-Ba(1)-F(2)#4	72.2(3)	F(2)-Ba(1)-Cl(1)#5	74.82(12)
F(2)-Ba(1)-F(2)#4	107.79(10)	F(2)#2-Ba(1)-Cl(1)#5	126.0(3)
F(2)#2-Ba(1)-F(2)#4	144.00(9)	F(2)#3-Ba(1)-Cl(1)#5	126.2(2)
F(2)#3-Ba(1)-F(2)#4	59.4(3)	F(2)#4-Ba(1)-Cl(1)#5	76.24(11)
F(3)#1-Ba(1)-F(1)#5	61.77(11)	F(1)#5-Ba(1)-Cl(1)#5	62.60(10)
F(2)-Ba(1)-F(1)#5	42.1(3)	F(1)-Ba(1)-Cl(1)#5	167.27(10)
F(2)#2-Ba(1)-F(1)#5	97.51(16)	Cl(1)#6-Ba(1)-Cl(1)#5	69.19(4)
F(2)#3-Ba(1)-F(1)#5	116.15(12)	Cl(1)-Ba(1)-Cl(1)#5	113.42(6)
F(2)#4-Ba(1)-F(1)#5	65.8(2)	F(3)#1-Ba(1)-Cl(1)#7	130.8(3)
F(3)#1-Ba(1)-F(1)	61.77(11)	F(2)-Ba(1)-Cl(1)#7	66.1(2)
F(2)-Ba(1)-F(1)	97.51(16)	F(2)#2-Ba(1)-Cl(1)#7	66.1(2)
F(2)#2-Ba(1)-F(1)	42.1(3)	F(2)#3-Ba(1)-Cl(1)#7	144.66(8)
F(2)#3-Ba(1)-F(1)	65.8(2)	F(2)#4-Ba(1)-Cl(1)#7	144.66(8)
F(2)#4-Ba(1)-F(1)	116.15(12)	F(1)#5-Ba(1)-Cl(1)#7	99.17(9)
F(1)#5-Ba(1)-F(1)	118.34(17)	F(1)-Ba(1)-Cl(1)#7	99.17(9)
F(3)#1-Ba(1)-Cl(1)#6	131.4(3)	Cl(1)#6-Ba(1)-Cl(1)#7	97.85(6)
F(2)-Ba(1)-Cl(1)#6	143.94(10)	Cl(1)-Ba(1)-Cl(1)#7	68.54(4)
F(2)#2-Ba(1)-Cl(1)#6	143.94(10)	Cl(1)#5-Ba(1)-Cl(1)#7	68.54(4)
F(2)#3-Ba(1)-Cl(1)#6	65.96(18)		
F(2)#4-Ba(1)-Cl(1)#6	65.96(18)	F(2)#9-B(1)-F(2)#2	116.3(8)

F(1)#5-Ba(1)-Cl(1)#6	117.43(9)	F(2)#9-B(1)-F(3)	113.7(5)
F(1)-Ba(1)-Cl(1)#6	117.43(9)	F(2)#2-B(1)-F(3)	113.7(5)
F(3)#1-Ba(1)-Cl(1)	123.28(3)	F(2)#9-B(1)-F(1)	101.1(9)
F(2)-Ba(1)-Cl(1)	126.0(3)	F(2)#2-B(1)-F(1)	101.1(9)
F(2)#2-Ba(1)-Cl(1)	74.82(12)	F(3)-B(1)-F(1)	109.1(7)
F(2)#3-Ba(1)-Cl(1)	76.24(11)		

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y+2,z-1/2; #2 -x+2,y,z; #3 -x+2,y,z-1; #4 x,y,z-1; #5 x+1,y,z; #6 -x+3/2,-y+1,z-1/2; #7 -x+3/2,-y+1,z+1/2; #8 x,y,z+1; #9 x-1,y,z; #10 -x+3/2,-y+2,z+1/2

Table S3. Anisotropic displacement parameters for $BaClBF_4$.

	U11	U22	U33	U23	U13	U12
Ba(1)	0.015(1)	0.012(1)	0.015(1)	0.000(1)	0	0
Cl(1)	0.015(1)	0.016(1)	0.018(1)	0.004(2)	0	0
B(1)	0.024(3)	0.016(3)	0.021(5)	-0.001(2)	0	0
F(1)	0.038(3)	0.032(2)	0.023(2)	0.000(2)	0	0
F(2)	0.024(2)	0.029(1)	0.047(3)	-0.004(3)	-0.014(5)	-0.008(1)
F(3)	0.038(2)	0.015(2)	0.050(2)	-0.008(6)	0	0

Table S4. Calculation detail of dipole moments for $BaCl_4F_7$ polyhedra.

	Distance from Ba	Bond valance	dipole moment				
						magnitude	
			x(*a*)	*y*(*b*)	*z*(*c*)	Debye	$\times 10^{-4}$ esu·cm/Å^3
Cl1	3.1271	-0.3035	-9.3186	-6.1174	0.1215	11.1479	963.52
Cl1$^{\#1}$	3.1653	-0.2737	0	-7.1265	8.2962	10.9369	945.28
Cl1$^{\#2}$	3.1139	-0.3145	0	-7.4363	-8.411	11.2271	970.36
Cl1$^{\#3}$	3.1271	-0.3035	9.3186	-6.1174	0.1215	11.1479	963.52
F1	3.0440	-0.0997	-4.8811	2.6900	1.1616	5.6931	492.05
F1$^{\#4}$	3.0440	-0.0997	4.8811	2.6900	1.1173	5.6842	491.29
F2	2.8923	-0.1502	3.05127	1.8786	4.8191	6.0053	519.04
F2$^{\#5}$	2.9665	-0.1229	2.8853	1.7764	-4.7374	5.8245	503.41
F2$^{\#6}$	2.9665	-0.1229	-2.8853	1.7764	-4.7374	5.8245	503.41
F2$^{\#7}$	2.8923	-0.1502	-3.0512	1.8786	4.8191	6.0053	519.04
F3	2.7067	-0.2481	0	6.7154	-0.0082	6.7155	580.42
Total	–	2.1892	0	-7.3919	2.5623	7.8235	676.19

Symmetry code: (#1) 1.5-*x*, 1-y, 0.5+*z*; (#2) 1.5-*x*, 1-*y*, -0.5+*z*; (#3) 1+*x*, *y*, *z*; , (#4) 1+*x*, *y*, *z*;

(#5) *x*, *y*, -1+*z*; (#6) 2-*x*, *y*, -1+*z*; (#7) 2-*x*, *y*, *z*.

Table S5. Calculation of dipole moments for $BaCl_4F_7$ and BF_4 polyhedra.

Species	Symmetry code of cations	dipole moment				
					magnitude	
		x (*a*)	*y* (*b*)	*z* (*c*)	debye	$\times 10^{-4}$ esu·cm/Å^3
$BaCl_4F_7$	*x*, *y*, *z*	0	-7.3920	2.5623	7.8235	676.19
	2.5-*x*, 1-*y*, 0.5+*z*	0	7.3920	2.5623		
BF_4	*x*, *y*, *z*	0	-0.7995	-4.6872	4.7549	410.97
	1.5-*x*, 2-*y*, -0.5+*z*	0	0.7995	-4.6872		
Unit cell	–	0	0	-4.4290	–	191.40

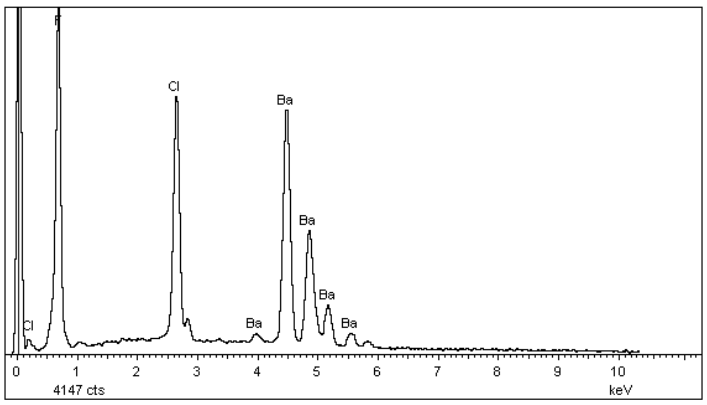
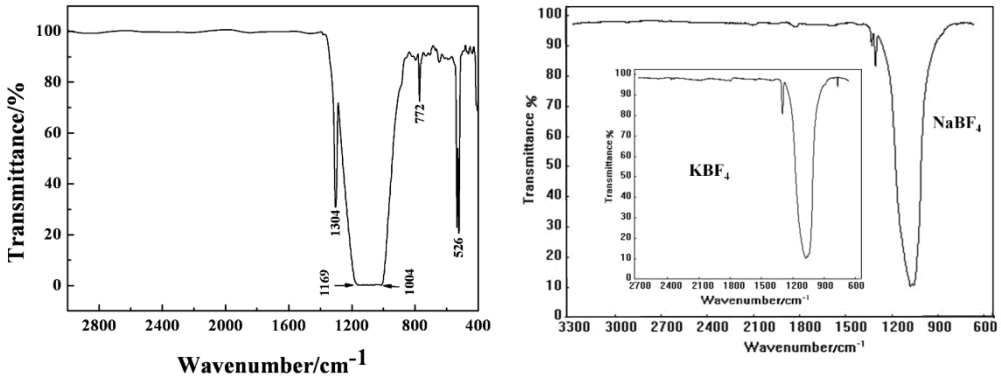


Fig. S1 EDS spectrum of $BaClBF_4$ sample.



(a) (b)

Fig. S2 IR spectrum of (a) $BaClBF_4$ (b) KBF_4 and $NaBF_4$.

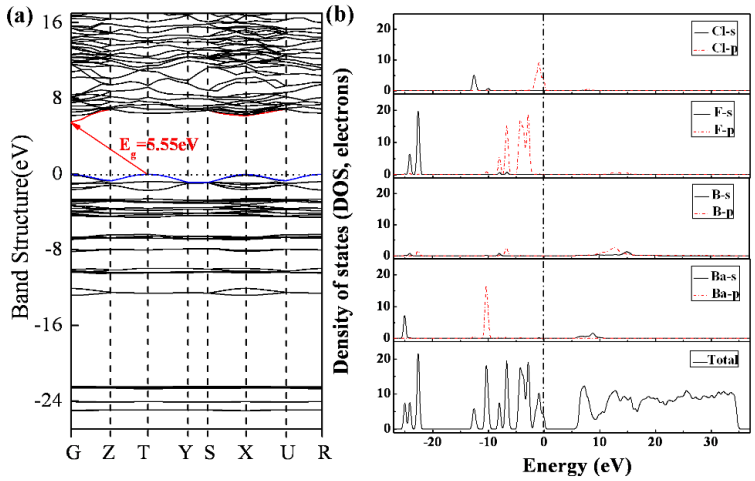


Fig. S3 Calculated band structure (a) partial density of states (b) for $BaClBF_4$.

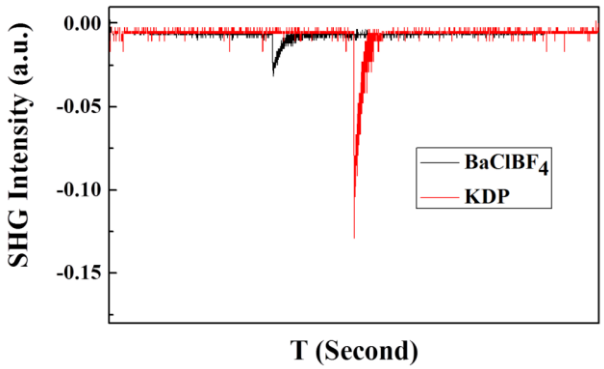


Fig. S4 Oscilloscope traces of the SHG signals for the powder (105-150 μm particle size range) of $BaClBF_4$ and KDP.

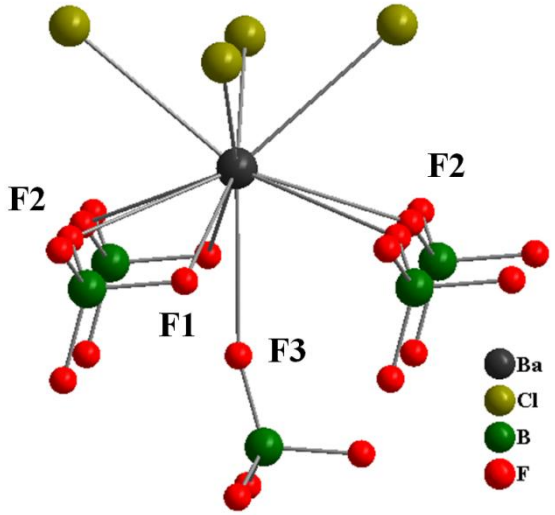


Fig. S5 The coordinates of Ba atom and B atom.